

Silicon isotopes indicate enhanced carbon export efficiency in the North Atlantic during deglaciation

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Abstract

Today's Sargasso Sea is nutrient-starved, except for episodic upwelling events caused by wind-driven winter mixing and eddies. Enhanced diatom opal burial in Sargasso Sea sediments indicates that silicic acid, a limiting nutrient today, may have been more available in subsurface waters during Heinrich Stadials, the millennial-scale climate perturbations of the last glacial and deglaciation. Here we use the geochemistry of opal-forming organisms from different water depths to demonstrate changes in silicic acid supply and utilisation during the most recent Heinrich Stadial. We suggest that during the early phase (17.5-18 ka), wind-driven upwelling replenished silicic acid to the subsurface, resulting in low Si utilisation. By 17ka, stratification reduced the surface silicic acid supply and increased Si utilization efficiency. This abrupt shift in Si cycling would have contributed to high regional carbon export efficiency during the recent Heinrich Stadial, despite being a period of increasing atmospheric CO₂.

Introduction

In the modern ocean, the North Atlantic subtropical gyre is classified as oligotrophic, with low surface nutrient concentrations and low annual primary productivity ¹. The Sargasso Sea, situated within the gyre, experiences a spring plankton bloom – despite being strongly and chronically Si limited ¹ - as a result of seasonal wind-driven deep mixing from the upper boundary of the main thermocline (Figure 1). However, the deep supply of nutrients supports a bloom that represents only a transient phytoplankton standing stock concentrated in a deep (~100 m) chlorophyll *a* maximum of up to ~0.5 mg m⁻³, a modest

amount compared to regions of the open Southern Ocean ($\sim 1 \text{ mg m}^{-3}$) and major upwelling zones and coastal areas (over 10 mg m^{-3}). In the Sargasso Sea, diatoms contribute strongly to export production, despite a significant proportion of primary productivity originating from smaller phytoplankton cells, as a result of a strong microbial loop¹. There have been substantial efforts in the last decade to understand the impact on modern ecology of nutrient upwelling driven by cyclonic and Mode-Water mesoscale eddies, the latter of which promotes the growth of larger sized phytoplankton (diatoms and dinoflagellates)³, but the role of these mesoscale processes in past carbon cycling and their potential impact in future global change remains unclear.

Multi-proxy evidence points towards a widespread increase in supply of Si(OH)_4 -rich waters during the abrupt climatic events of the last glacial and deglacial, including the Southern Ocean⁴, equatorial regions⁵, and major coastal upwelling zones⁶. Sedimentary evidence also points towards anomalous and prolonged diatom blooms in the North Atlantic during abrupt events of the deglacial^{7,8}, which would have had a significant impact on carbon cycling in the otherwise oligotrophic gyre. During the last glacial and deglaciation, the climate was punctuated by abrupt millennial-scale Heinrich Stadials (HS) associated with ice-berg rafting events in the North Atlantic that led to widespread and rapid reorganization of ocean circulation that resulted in shifts in heat transport, atmospheric pCO_2 , and the supply of southern component water to northern latitudes⁹.

Southern component water plays an important role in the supply of essential nutrients such as silicic acid (Si(OH)_4), which feeds the diatom growth that contributes significantly to marine carbon export production in the world's oceans. Antarctic Bottom Water (AABW), formed by deep convection around Antarctica, contains high levels of macronutrients including Si(OH)_4 ($>100 \text{ } \mu\text{M}$ ¹⁰). Antarctic Intermediate Water (AAIW), formed by the subduction of cold, fresh surface waters near the Polar Front, has low Si(OH)_4 concentrations ($< 70 \text{ } \mu\text{M}$, generally $\sim 40 \text{ } \mu\text{M}$ north of 20°S) compared to other nutrients (nitrate and phosphate) as a result of efficient uptake of Si by diatoms in the Southern Ocean¹¹, and can influence the nutrient content of the thermocline in the South Atlantic through mixing across density surfaces¹².

There has been recent debate about the degree to which AAIW extent and composition fundamentally changed during the millennial scale climate events of the late glacial/deglacial, the role played by wind-driven versus oceanographic processes in these changes, and the impact of these changes on diatom productivity (reviewed by ⁸). Neodymium isotope evidence points both towards a volumetric increase in AAIW at intermediate depths of the Equatorial regions ^{13,14}, but also a decline in AAIW in the Florida Straits during HS1 ¹⁵. Nutrient proxies cannot determine the origins of the water, but do indicate that the mid-depths of the South Atlantic were more enriched in Si(OH)_4 relative to other nutrients than it is today ^{16,17}, and suggest a northwards advance of AAIW into the North Atlantic during HS1 ¹⁸.

Although there is evidence for increased diatom opal burial in the oligotrophic North Atlantic during stadials ⁷, there has been as yet no quantified study of low-latitude silicon cycling during millennial scale climatic change, and its impact on carbon cycling. Here, we use the silicon isotope composition of different opal-forming organisms, extracted from a sediment core in the Sargasso Sea, that dwell at different depths in the water column to reconstruct changes in Si cycling during the last deglaciation. Our results show that there were abrupt shifts in Si supply and utilisation during this period, consistent with changes in water stratification, that would have contributed to high regional carbon export efficiency.

Results

Opal producing organisms from the Sargasso Sea sediment core

Core HU89038-PC8 on the Bermuda Rise (33.7 °N, 57.6 °W, 3.5 km water depth) contains a notable opal-rich section radiocarbon dated to HS1 (from 330-500 cm depth, or 16.5-18.6 calibrated ka ¹⁹. The sand fraction of the opal-rich layer comprises 60±10% opal, and is dominated (~95%) by fragments of the large diatom *Ethmodiscus rex* (Rattray) Hendey, with radiolarians, smaller diatoms and rare sponge spicules. *E. rex* are relatively deep-dwelling, occupying a distinct niche by opportunistically migrating deeper (> 100 m) through varying their cellular buoyancy to take advantage of deep nutrient supplies, and are

found today in the oligotrophic gyre of the North Pacific in highly stratified waters away from major convergence zones²⁰. *E.rex* cells subsequently undergo mass sinking at frontal zones, or when stratification is broken by another physical mechanism, such as storm mixing²¹. Most polycystine radiolarians live in water depths of less than 250m and this is especially true for large open-structure Spumellaria, which often have associated with them symbiotic algae (zooxanthellae) and must spend at least some time in the euphotic zone to survive. The most common radiolarians picked from the sediments in this study (see methods) have all been recovered from depths between 100-390 m in the modern. The information available suggests that most, if not all, of the large Spumellaria analyzed spent most of their lives in waters shallower than 250m and possibly less than 100m.

Whilst the presence of the *E.rex* layer in HU89038-PC3 is in itself suggestive of an unusual and prolonged shift in biogeochemical cycling during HS1, we can also quantify the silicon biogeochemical system using the silicon isotope composition of different siliceous plankton opal that live at different depths in the water column. The silicon isotope ($\delta^{30}\text{Si}$) of diatoms can be used as a measure of Si utilisation in ambient seawater because preferential uptake of the lighter isotope of Si leads to progressive enrichment in the heavier isotopes²². Diatom material was sufficiently abundant in this section of HU89038-PC8 such that it was possible to hand-pick monospecific samples of *E.rex* and mixed samples of polycystine radiolarians, mostly large Spumellaria, for silicon isotope analysis (see methods). The *E. rex* $\delta^{30}\text{Si}$ ranged from +0.20 to +1.14 ‰, and the mixed Spumellaria radiolarian $\delta^{30}\text{Si}$ ranged from +0.73 to +2.00 ‰. Full results are given in Supplementary Table S1.

Spicule record from the Carolina Slope

Our new diatom and radiolarian silicon isotope records provide information on the utilisation of Si in surface waters of the Sargasso Sea, but an integrated view of a biogeochemical system relies on the robust quantification of inputs and outputs of essential nutrients, in this case $\text{Si}(\text{OH})_4$. Mid-depth benthic $\text{Si}(\text{OH})_4$ concentrations of waters feeding the North Atlantic subtropical gyre were reconstructed using the $\delta^{30}\text{Si}$ composition of abundant and well-preserved sponge spicules extracted from marine sediment core KNR140-2-56GGC from the Carolina Slope (32°56.3'N, 76°17.7'W; 1400 m; Figure 1). The $\delta^{30}\text{Si}$ of seafloor-dwelling sponges has been shown to be a proxy for benthic $\text{Si}(\text{OH})_4$

concentrations as a result of enhanced uptake and associated fractionation of Si under higher Si(OH)_4 concentrations²³. Downcore sponge spicule $\delta^{30}\text{Si}$ from KNR140-2-56GGC ranged from -1.22 to -1.93 ‰ (Figure 2; Supplementary Figure S1, S2). The average $\delta^{30}\text{Si}$ value of the Holocene (<10 ka, 0-400 cm) spicules extracted from KNR140-2-56GGC was significantly heavier (1SD) than that of samples deeper than 400 cm (>10 ka), signifying that the sponges growing in the Holocene experienced lower ambient Si(OH)_4 conditions, on average, than sponges growing in the late glacial and deglacial (Figure 2; Supplementary Figure S1). The modern core-top $\delta^{30}\text{Si}$ value corresponds to ambient Si(OH)_4 concentrations of approximately 15-20 μM (www.ewoce.org), matching modern observations at these depths and indicating a minimal impact of downslope transport on the spicule proxy. The mean Holocene value of spicule $\delta^{30}\text{Si}$ corresponds to a Si(OH)_4 concentration of $\sim 25 \mu\text{M}$ (Figure 2). Our record shows lighter $\delta^{30}\text{Si}$ values, and therefore a higher Si(OH)_4 concentration (30-37 μM), corresponding to HS1 (~ 15 -18 ka). The higher Si(OH)_4 values could result from the diffusion of nutrients from underlying AABW⁸. Today the core is bathed in NADW, and proxy-based reconstructions suggest intermediate depth waters of the North Atlantic were bathed in Glacial North Atlantic Intermediate Water (GNAIW) during the glacial²⁴. Physical and chemical properties of North Atlantic sediment cores indicate that there was a weakening of GNAIW flow during HS1²⁵, stagnation of intermediate waters, and a shoaling of southern sourced abyssal water to within $\sim 1000\text{m}$ of our core site²⁶. Alternatively, it is possible that the higher Si(OH)_4 concentrations at our core site during HS1 were a result of northwards flow of AAIW. The higher concentration of Si(OH)_4 supplying the intermediate depths of the North Atlantic during millennial scale climate events is similar in magnitude to a previous reconstruction of South Atlantic intermediate depth Si(OH)_4 concentrations, and is consistent with cross-equator flow of southern-sourced waters into the North Atlantic during HS1¹⁷. Sedimentological properties of cores from the Carolina Slope indicate that the upper boundary of the GNAIW may have been deeper than 1400m before the Holocene, as indicated by a low content of red material that characterised sediments from the Labrador Sea (Supplementary Figure S3,²⁷). Furthermore, the increase in Si(OH)_4 recorded at our core site is relatively modest, and reflects concentrations more typical of AAIW (<70 μM) rather than AABW (>100 μM).

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In order to quantify the efficiency of surface utilisation of $\text{Si}(\text{OH})_4$ in the Sargasso Sea using core material from HU89038-8PC, it is necessary to quantify the silicon isotope fractionation by both *E. rex* and Spumellarian radiolarians. Laboratory culture studies of diatoms of other genera indicate a mean fractionation of -1.1‰ ²² and show some limited evidence for variation with species and growth rate²⁸. Although they may represent specific growth conditions, by using a monospecific sample in this study we have eliminated any bias as a result of changing diatom assemblage over time and have quantified Si uptake by the likely dominant species (*E. rex* representing ~95% of the opal fossils present in the HS1 layer). Measurements of $\delta^{30}\text{Si}$ on the >63 micron opal fraction matched the *E. rex* within error, demonstrating that *E. rex* likely dominated opal production during this interval. The radiolarians in core HU89038-PC8 have a highly enriched $\delta^{30}\text{Si}$ signal (Figure 3). Assigning a fractionation factor of -1.1‰ , we can model the utilisation by *E. rex* using isotope fractionation equations²⁹, which yields a resulting water Si isotope composition of approximately $+2.3\text{‰}$ (from ~18 ka BP) to $+3\text{‰}$ (from ~16.5 ka BP) and a radiolarian fractionation factor of approximately -1 to -2‰ , consistent with the limited previous data (see methods section for details)³⁰. If the two groups were growing from the same unaltered seawater (intermediate depth North Atlantic water or AAIW both have a $\delta^{30}\text{Si}(\text{OH})_4$ of $\sim +1.6\text{‰}$, see methods), the radiolarians would be positively discriminating against the lighter isotope of silicon during some time periods (e.g. ~17 ka BP), which is not known in any biological system. This separation of radiolarian and diatom Si uptake could have occurred if either the radiolarians and diatoms are growing in a similar water mass but *E. rex* take up the silicon sufficiently rapidly such that they control the silicon chemistry of the seawater, or the radiolarians are not growing at the same depth as the *E. rex* cells. Either mechanism would imply that the radiolarians grew in water already isotopically enriched by *E. rex*. The radiolarian $\delta^{30}\text{Si}$ signal also showed less variability than the *E. rex* signal, possible due to temporal or spatial averaging over a season or different depths as a result of the mixed assemblage of radiolarians used for analysis.

We quantified this system further using a simple fractionation model (see methods), feeding *E. rex* with $\text{Si}(\text{OH})_4$ from thermocline waters assuming an open system²⁹ and a fractionation factor of -1.1‰ ²⁰. The remaining $\text{Si}(\text{OH})_4$ not utilized by the *E. rex* was then supplied to the radiolarians, which fractionate Si in an isotopically closed system. The

calculated utilisation does not change significantly when the assumed fractionation factor for radiolarians is varied within reasonable boundaries. At the beginning of HS1, *E. rex* utilised a negligible proportion of the Si(OH)_4 available, suggesting some other factor limited production, and the radiolarians utilised approximately 40%. By 17 ka the *E. rex* and radiolarians were utilising up to 50% and 100% of the Si(OH)_4 available to them respectively (Figure 3), suggesting total Si(OH)_4 utilization. Such large and rapid changes in utilisation exceeded any deglacial change in Si utilisation in the Southern Ocean or Eastern Equatorial Pacific upwelling zones^{31,32}, and are indicative of significant changes in wind stress and buoyancy forcing at the inception of HS1.

We can use the simple Si isotope fractionation model (after²²) to provide quantitative limits on the opal production and export rates during the utilisation peak of the HS1 diatom event. Today, the Si(OH)_4 concentrations of sub-thermocline waters in the North Atlantic are approximately 15-20 μM , and mix into the subsurface waters to provide $\sim 1.5 \mu\text{M}$ Si^1 . Our sponge spicule $\delta^{30}\text{Si}$ results from KNR140-2-56GGC indicate that 30 μM Si were available for biological uptake in sub-thermocline during HS1, suggesting subsurface waters would have a concentration of $\sim 2\text{-}3 \mu\text{M}$ Si assuming similar advection and diffusion rates as today. For an upwelling water supply rate of $1 \text{ m}^2 \text{ day}^{-1}$ ³³, our calculations suggests that $\sim 20 \text{ mmol Si m}^{-2} \text{ day}^{-1}$ were utilized during this time period, although it is possible that there were variations in Si(OH)_4 concentration of sub-thermocline waters that have not been detected by our spicule record (Figure 2). Assuming 50% of the opal is recycled in the subsurface (the global average³⁴), we estimate a total of approximately $10 \text{ mmol Si m}^{-2} \text{ day}^{-1}$ was exported to the deep ocean at the inception of HS1, compared to $\sim 1.3 \text{ mmol Si m}^{-2} \text{ day}^{-1}$ today in a Mode-Water eddy driven bloom³⁵. A more sophisticated two box biogeochemical model achieves similar opal output fluxes (see methods, Supplementary Figures S4,S5).

Discussion

The assemblage composition and isotopic signals from the diatoms and radiolarians indicate an environmental setting in which upwelling Si(OH)_4 -rich waters are utilized at depths greater than 100 m by *E. rex* with radiolarians (and small diatoms) taking up the isotopically enriched Si(OH)_4 “leftovers”. How could such a scenario evolve? *E. rex* require

strong stratification to dominate ecosystems, with a breakdown in stratification triggering sinking and sedimentation ²¹. It is possible that the enhanced Si(OH)₄ concentrations within the thermocline that occurred as a result of changes in ocean circulation at the inception of HS1 (17.5-18 ka) could have promoted giant diatom species such as *E. rex*, in a similar way to the modern North Pacific. The frequent replenishment of nutrients resulted in the sinking of the *E. rex* cells into the deep ocean and, therefore, low Si utilization. Rapid sinking and sedimentation of the *E. rex* cells would then have been promoted by deep mixing, which could have been caused by enhanced wind-stress as observed for other Heinrich Stadials pre-30 ka ³⁶, turbulent mixing due to ice-bergs, or upwelling at an unstable oceanic front ³⁷. A review of core descriptions reveals that the occurrence of *E. rex* during the deglacial appears to be limited to a region of approximately 100-200 km diameter near the Bermuda Rise (Supplementary Figure S6) that could be indicative of a mesoscale forcing mechanism, concentrating the cells into a particular region, rather than a large-scale shift in frontal systems. Today, wind-driven mesoscale processes are known to extend to at least 1000m depth ³⁸, bringing up deep sources of nutrients and driving phytoplankton blooms that are as strong as the spring blooms driven by seasonal wind-driven deep mixing (Figure 1). In particular, Mode-Water eddies are known to drive changes in ecology, promoting large diatom production in the Sargasso Sea e.g. *Chaetoceros* ³⁵. Rapid sinking and sedimentation of the *E. rex* cells could therefore have been promoted during early HS1 by periodic eddy processes, due to wind or ice-berg forcing, which would also have replenished nutrient supplies to the subsurface.

By 17 ka, a progressive increase in stratification may have led to higher Si utilization in surface waters, as a result of meltwater, reduced wind stress or frontal zone convergence. In the Sargasso Sea, stratification is unlikely to have resulted from a reduction in wind stress during HS1 ³⁶, or from the convergence of frontal systems. Introduction of meltwater lenses during ice-rafting events are consistent with records of smaller diatoms ⁷ and the deposition of ice-rafted debris (IRD) at the Bermuda Rise ⁹, and the onset of changes in the planktonic foraminiferal $\delta^{18}\text{O}$ record from HU89038-PC8 (Figure 3). The high percentage counts of the deep-dwelling radiolarian *Cycladophora davisiana* Ehrenberg observed near the top of the section indicate that periodic and intense upwelling still occurred, albeit at a lower frequency, replenishing the nutrient supply and promoting more occasional *E. rex* sinking

and sedimentation. *E. rex* production continued until either stratification broke down, or thermocline Si concentrations declined and a system similar to the modern was established.

Comparing the results from the simple fractionation model to sedimentary opal accumulation rates from the Bermuda Rise shows that the increase in export of opal from the subsurface/thermocline to deep waters was greater than the increase in opal burial, indicating deep opal remineralisation and a reduction in the burial efficiency (Table 1). Low resolution data for a nearby core on the Bermuda Rise (GGC5 and WHOI long core CDH19 Henry, McManus et al., unpublished data) indicate that the thorium-normalised Holocene sediment flux is $\sim 2 \text{ g cm}^{-2} \text{ ka}^{-1}$, of which 4-5 % is opal, giving a sedimentary opal flux of $< 0.1 \text{ g SiO}_2 \text{ cm}^{-2} \text{ ka}^{-1}$. In contrast, the opal percentages at HS1 and the LGM were approximately 6-8% and 4-6% respectively, with HS1 and LGM thorium-normalized sediment accumulation rates of $3.7 \text{ g cm}^{-2} \text{ ka}^{-1}$ and 5.6 g cm^{-2} respectively, giving sedimentary opal fluxes of approximately $0.25 \text{ g SiO}_2 \text{ cm}^{-2} \text{ ka}^{-1}$ for HS1 and $0.28 \text{ g SiO}_2 \text{ cm}^{-2} \text{ ka}^{-1}$ for the LGM (Table 2). The Holocene sedimentary opal flux equates to a little more than $\sim 10 \text{ mmol Si m}^{-2} \text{ yr}^{-1}$, which represents a preservation efficiency of approximately 20% of the observed sinking flux of $50 \text{ mmol Si m}^{-2} \text{ yr}^{-1}$ of opal from surface to deep waters¹. Our estimated HS1 sedimentary opal flux is more than double that of the Holocene or modern. The greater abundance of *E. rex* the diatom assemblage did not appear to markedly increase the opal flux to the sediments at HS1 compared to the preceding LGM. However, observations and modeling of the modern ocean indicate that in regions where large diatoms grow, the increase in export due to rapid sinking of material out of the surface ocean is accompanied by an increase in deep remineralisation³⁹. The HS1 sedimentary opal flux equates to a little less than $\sim 40 \text{ mmol Si m}^{-2} \text{ yr}^{-1}$, which - depending on the assumed length of the bloom (~ 30 days) - is consistent with a lower preservation efficiency of approximately 10-15% of the opal exported out of surface waters from our model simulations (i.e. total preservation efficiency of ~ 5 -10%). Because the order of magnitude increase in overall sediment accumulation rates at that time should have strongly enhanced the preservation potential of opal deposited on the seafloor, it appears likely that greater dissolution occurred in the mid-depth to deep ocean. This dissolution may have had an influence on the assemblage of opal fossils preserved, although smaller diatoms and delicate radiolarians are still present in the opal-rich layer of HU089038.

High export of opal into deep waters would have been accompanied by an increase in carbon export (see methods). *E. rex* are also found from a similar time in a nearby core OCE326-5GGC during a period of relatively low ^{230}Th -normalised carbonate flux, indicating diatom productivity was promoted without a relative increase in productivity of carbonate producers⁹. This shift towards opal producers relative to carbonate-secreting phytoplankton would have resulted in at least a localized change in ocean alkalinity acting to further drawdown CO_2 in the near-surface waters⁴⁰.

Palaeoceanographic records show that during the deglacial there were widespread pulses of diatom production, which we suggest were due to the abrupt breakdown of stratification, similar to - but to a greater extent than - today, as a result of different wind-driven mechanisms linked by atmospheric teleconnections, which supplied nutrients to large regions of the surface ocean, rather than slow diffusion processes^{4-6,31,41}. The *E. rex* pulse studied here either occurs at a similar time as, or at the inception of, increases diatom accumulation throughout Atlantic upwelling regions (e.g. Northwest Atlantic^{6,8,42}). This upwelling, together with an increase in thermocline Si(OH)_4 concentration, stimulated widespread diatom productivity and enhanced Si utilisation (Figure 3). These wind-driven processes in the low-latitudes of the Atlantic and Pacific appeared to occur approximately concurrently and early in HS1^{5,14,43} at the onset of the significant changes in upwelling that occurred in the Southern Ocean (Figure 3). Assuming these offsets are real, and not a result of uncertainties in the age models, they could highlight the importance not only of global changes in preformed nutrients, but also more localized processes that allow these preformed nutrients to reach the surface, which drove ecological regime shifts and marine carbon uptake. The early upwelling signal in some regions of the low latitudes, at the onset of the significant changes in upwelling that occurred in the Southern Ocean (Figure 3), suggests climatic changes in the North Atlantic were transferred to the southern hemisphere via atmospheric and oceanic teleconnections, at the same time as the initiation of the pCO_2 rise recorded in ice cores (Figure 3). Despite such high biological productivity, physical changes in ocean circulation and subsequent release of stored carbon overwhelmed any biological response, leading to a rise in pCO_2 ⁴.

Methods

Silicon isotope measurements

Sponge spicules were hand-picked from the sand fraction ($> 63\mu\text{m}$) of core KNR140-2-56GGC and cleaned according to ²³. For HU89038 -8PC, the opal content of the ~300-500cm section was removed from the sand fraction, which constitutes a relatively small proportion of the sediment, using flotation, in order to pick foraminifera for analyses ¹⁹. These biogenic opal fractions were cleaned initially using a filtration method adapted from ⁴⁴. Briefly, the samples were suspended in deionized water and poured into a cylindrical filter funnel, fitted with a 200 micron filter mesh at the base, which was clamped into a water bath. The whole apparatus was placed in an ultrasonic bath and sonicated for at least half an hour, flushing through the sample with at least 1L of deionized water. This method removes the smaller grains of pyrite and removes particles adhered to the opal leaving a clean biogenic component. The filter mesh was removed from the apparatus, and the different biogenic components were hand-picked: 1) large Spumellaria radiolarians (dominated by relatively shallow dwelling forms, see below); and 2) a monospecific sample of *E. rex* fragments. Smear slides were made of the >63 micron fraction for radiolarian counts and species identification.

The different biogenic opal components were rinsed in deionized water, dried down in Teflon vials, then dried down again in distilled concentrated HNO_3 at 180°C . Whilst still hot, 500 μL of 0.4M NaOH were added to each sample, and dissolved over one day (in the case of *E. rex* samples) or three days (in the case of the radiolarians and sponges) at 100°C . The samples were acidified using 0.2N in-house Teflon distilled HCl, and purified using cation exchange resin according to ⁴⁵. The samples were analyzed for silicon isotope composition using the Neptune Multi-Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS) at the WHOI Plasma Facility. Mass bias and matrix effects were corrected using internal Mg-doping according to ⁴⁶. The results are reported as $\delta^{30}\text{Si}$ values related to the standard NBS28. Repeat measurements were carried out for all the samples (typically $n=3$, depending on sample availability) and the mean isotope ratio calculated in each case. Long-term external reproducibility was assessed by measuring the $\delta^{30}\text{Si}$ of a biogenic opal standard ⁴⁷ over several months. The reproducibility of the mean $\delta^{30}\text{Si}$ (-3.43‰) from the repeat measurements of the standard each run using the Mg-doping method was $\pm 0.1\text{‰}$ (2SD). The repeat measurements carried out for the samples also generally agreed within $\pm 0.1\text{‰}$ or better. A three-isotope plot ($\delta^{29}\text{Si}$ vs. $\delta^{30}\text{Si}$) of all of the opal samples measured in this study fall on a straight line through the origin with a gradient of approximately 0.51, indicative of mass dependent fractionation (Supplementary Figure S2).

Two >63 micron opal fraction samples from HU89038-8PC (from ¹⁹) were measured to investigate the impact that the other siliceous species, in addition to *E. rex*, had on $\delta^{30}\text{Si}$. The samples were heated in H_2O_2 (30%), dried and then fused with NaOH pellets in silver crucibles at 730°C for 10 minutes. The fusion cake was cooled briefly, then quenched in 18 M Ω .cm Milli-Q water, left overnight and acidified with 2N in-house Teflon distilled HCl. The solutions were purified by cation exchange resin as above and measured for silicon isotopes by MC-ICP-MS without Mg correction (external reproducibility $\sim 0.16\text{‰}$ for $\delta^{30}\text{Si}$ ⁴⁷). By preparing these samples using a different method, we can show there is no analytical bias introduced through choice of sample dissolution process.

Radiocarbon measurements

The age model for KNR140-2-56GGC was based on existing planktonic foraminiferal radiocarbon measurements and an additional five radiocarbon measurements (Supplementary Table S2) of *Globigerinoides ruber* (white) picked (greater than 150 µm size fraction) measured at the National Ocean Sciences Accelerator Mass Spectrometry facility at Woods Hole Oceanographic Institution (NOSAMS). Calendar ages were calculated using Calib v. 6.1.0, using Marine09 and a ΔR of 148 (± 70).

The age model for HU089038-8PC was based on radiocarbon measurements obtained from ¹⁹.

Radiolarian depth of habitat

Most polysystine radiolarians live in water depths of less than 250m and this is especially true for the Spumellarians (spherical shelled species) ^{48,49}. The specimens analyzed in this study are large (>100µm), frequently spongy, Spumellarians. The large spongy species belong to the genera *Spongechinus*, *Spongodymus* and *Plegmosphaera*. *Spongodymus* and other large spongy Spumellarians often have associated with them symbiotic algae (zooxanthellae) ⁵⁰. For these symbionts to thrive the host radiolarians must spend some time within the euphotic zone. The most common radiolarian in the assemblage, *Actinomma medianum* (Haeckel), has been recovered from water depths of less than 100m in the eastern Pacific ⁵¹. Other Spumellarians include *Acanthosphaera actinota* (Haeckel) which was raised from less than 100m in numerous plankton samples from the California Current system ⁵¹, *Actinomma arcadophorum* (Haeckel) and a species of *Hexactinium* probably, *H. axatrias* (Haeckel), reported by ⁵², together with the former two, from the shallowest (389m) of a series of sediment traps moored in the western equatorial Atlantic. Although precise depth ranges for the radiolarian species analyzed in this study are not known the information available suggests that most, if not all, of the large Spumellarians analyzed spent most of their lives in waters shallower than 250m and possibly less than 100m.

Calculating utilisation

Utilisation was calculated for the *E.rex* and radiolarians assuming open fractionation²⁹:

$$f=1-(\delta_{opal}-\delta_{Si(OH)_4})/\varepsilon \quad (1)$$

where f = utilisation, δ_{opal} = silicon isotope composition of the opal, $\delta_{Si(OH)_4}$ = the silicon isotope composition of the input seawater (assumed to be +1.6 per mil, for either North Atlantic or AAIW ⁵³), and ε = fractionation by opal producing organisms (assumed to be -1.1 per mil). The Si isotopic composition of AAIW was assumed to be constant during this period, due to a lack of significant change in diatom $\delta^{30}Si$ from the subantarctic during this period ⁵⁴.

The remaining seawater composition was calculated according to Equation 2:

$$\delta_{Si(OH)_4}'=\delta_{Si(OH)_4}-\varepsilon f \quad (2)$$

HS1 Biogeochemical Model

A simple box model of biogeochemical cycling in the Sargasso Sea was created using Stella (version 9.1) based on the schematic shown in Supplementary Figure S4. Details of the variables used are in Supplementary Table S3 ^{55,56}. The model comprises two boxes, an intermediate box (below 100m

water depth) inhabited by diatoms and a shallow box (0-100m water depth) inhabited by radiolarians. The intermediate box is connected to an input from underlying thermocline waters. The intermediate and shallow boxes are linked by diffusive and advective pathways, according to the water column structure. The shallow box can additionally lose water through lateral transfer. To simplify the model, no lateral transfer is assumed for the intermediate box.

For any box i of volume V_i , change in concentration (C_i) is equal to the difference in the flux (F) in of Si and the flux out of Si.

An initial state of strong stratification exists and no initial Si is available in either box. Thermocline waters have a concentration of 30 μM Si. At $t=0$, diffusion and advection is turned on between the thermocline and the two boxes. Flux by diapycnal diffusion (across isopycnals), F_{vd} , is modeled assuming the isopycnals are nearly horizontal (Equation 3). Eddy diffusive mixing (along sloping isopycnals) is assumed to be negligible. Advection is dominated by large scale Ekman pumping, with the possibility of ageostrophic flow^{33,57}.

$$F_{vd} \sim -K_d \Delta C / \Delta z \quad (3)$$

Where K_d is the Diapycnal turbulent diffusion coefficient and z is depth.

E. rex is allowed to grow in the intermediate box, and radiolarians are allowed to grow in the surface box, with Si utilization constrained with the silicon isotope data from core HU89038-8PC. Fractionation of Si isotopes is calculated for each organism according to Equations 1 and 2. Opal flux (ϕ) is given by Equation 4 and depends on the utilization (f), the amount of Si available (C_i) and the proportion of opal that undergoes dissolution ($1-P$).

$$\phi = C_i \cdot f \cdot (1-P) \quad (4)$$

Carbon fluxes are calculated assuming Si:C ~ 0.13 mol/mol⁵⁸. The impact of isotopic fractionation⁵⁹ during dissolution was tested (percentage dissolution based on⁶⁰). The silica flux was sensitive to the advective flux (Supplementary Figure S5A), but was not sensitive to dissolution (Supplementary Figure S5B).

The fractionation factor for *E. rex* was allowed to vary between -0.9 and -2.1 ‰; the fractionation factor for Spumellaria radiolarians was allowed to vary between -1.1 and -2.1 ‰. Total silica flux and concentration was not sensitive to the fractionation factors used. Surface utilisation was sensitive to the fractionation factors selected (Supplementary Figure S5C).

Our estimate of mean daily sinking opal flux during the utilisation peak of HS1 from the model is the same order of magnitude as the total annual flux driven by modern winter convection today. The increased supply is due to a combination of intense stratification, punctuated by mesoscale processes, and the widespread increase in thermocline Si(OH)₄ concentrations resulting from the enhanced contribution of southern component water to the North Atlantic. The increase in diatom production would also have led to an increase in the carbon export production, and so CO₂ drawdown, to deep waters. For a typical Si:C molar ratio of 0.13⁵⁸, the model gives a total carbon flux of approximately 15 g C m⁻² day⁻¹. For *E. rex* growing over the period of a month, and with a high export efficiency typical of diatom dominated ecosystems, this sinking could result in carbon export

417 to deep waters of approximately $300\text{--}400 \text{ g C m}^{-2} \text{ yr}^{-1}$ during HS1, which is over an order of magnitude
418 greater than the export in the Sargasso Sea today ⁵⁸ ($\sim 10 \text{ g C m}^{-2} \text{ yr}^{-1}$).

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End notes:

Acknowledgements

The authors would like to acknowledge L. Gene Henry for sharing unpublished opal percentage and flux data. The authors would like to thank Tamara Catanach and Maureen Auro (WHOI) for assistance in the laboratory, Lloyd Keigwin and Alan Kemp for samples and discussion. Silicon isotope analyses were carried out at the WHOI ICP Facility, with the assistance of Jerzy Blusztajn and Scot Birdwhistell. KRH and LFR are funded by US National Science Foundation (US-NSF) grant MGG 1029986; KRH is supported by the Climate Change Consortium of Wales (C3W),

599 **The Royal Society and a UK NERC New Investigator Grant; LFR is supported by an European**
600 **Research Council Grant 278705; JFM is funded by US-NSF.**

601

602 **Author Contributions**

603 **KH carried out the isotopic analyses; JH assisted with radiolarian and diatom identification;**
604 **KH and LR wrote the manuscript, with significant contributions from JM and JH.**

605

606 **Competing Financial Interests**

607 **The authors declare no competing financial interests.**

608 **Figure Legends**

609 **Figure 1: Map showing the key localities for this study.** a) The stars show the localities of the
610 Bermuda Time Series (BaTS) site, and new sediment core records discussed in this study.
611 Note that OCE326-GGC5 was collected from the Bermuda Rise, very near the same location
612 as HU89038-8PC. The colour contours show the concentration of Si(OH)_4 in μM at 100m,
613 created using data from [10](#) and Ocean Data View (version 4). b) Chlorophyll *a* data from the
614 BaTS site from 1990-2005. The white arrows show documented eddies from the BaTS site ³,
615 and the black arrow shows a documented cold core ring during the EDDIES cruises ⁵⁵: c)
616 Si(OH)_4 concentrations at the BaTS site from 1990-2005, with arrows showing the drawdown
617 of upwelled Si(OH)_4 due to biological uptake (note different scale to a); (all data are from [60](#)).

618 **Figure 2: Results from sediment core KNR140-2-56GGC.** A) Greenland ice core records of
619 $\delta^{18}\text{O}$ ⁶¹, B) marine sediment $^{231}\text{Pa}/^{230}\text{Th}$ from the Bermuda Rise ^{10,62}, and C) $\delta^{18}\text{O}$ of
620 *Globigerinides ruber* from KNR140-2-56GGC ²⁷. D) The silicon isotope composition of the
621 spicules plotted against age from 0-25 ka (solid symbols and lines), together with the
622 reconstructed Si(OH)_4 concentration for core KNR140-2-56GGC (hollow symbols, dotted
623 lines), calculated assuming $[\text{Si(OH)}_4] = 270 / (\Delta\delta^{30}\text{Si} + 6.54) - 53$ ²³, where $\Delta\delta^{30}\text{Si}$ is the difference
624 in isotopic composition of the sponge spicules and seawater and assuming $\delta^{30}\text{Si(OH)}_4$ of
625 dissolved silicon in seawater is +1.6‰. The pink line shows the mean Holocene spicule $\delta^{30}\text{Si}$
626 (solid) and 1σ standard deviation (dashed). All error bars show $\pm 2\sigma$ standard deviation
627 unless stated otherwise. The triangles show radiocarbon tie points (Supplementary Table
628 S2). Vertical cyan bars show YD = Younger Dryas; HS1 = Heinrich Stadial One.

629 **Figure 3: Results from sediment core HU89038-8PC.** A) Silicon isotope results from sediment
630 core HU89038-8PC (error bars show $\pm 2\sigma_{\text{SD}}$). The solid squares show $\delta^{30}\text{Si}$ of *Ethmodiscus rex*
631 diatoms; the hollow squares show $\delta^{30}\text{Si}$ of Spumellarian radiolarians; the grey squares show
632 $\delta^{30}\text{Si}$ of >63 μm opal. There is a positive correlation between the *E. rex* and radiolarian $\delta^{30}\text{Si}$
633 measurements (Pearson correlation coefficient $R = +0.71$, $n = 10$, $P = 0.02$). The >63 μm opal
634 $\delta^{30}\text{Si}$ matched the *E. rex* opal $\delta^{30}\text{Si}$ from the same depth within error, which would be
635 expected given that *E. rex* constituted over 95% of the bulk opal. The lines show calculated
636 utilisation of Si by the *E. rex* (solid line) and radiolarian (dashed line) cells respectively, using
637 a fractionation factor of -1.1 ‰ for the *E. rex*. We plot the mean utilisation calculated for

638 radiolarians with fractionation factors ranging from -0.9 to -2.1 ‰ (Methods). B) The cyan
639 circles show planktonic foraminifera $\delta^{18}\text{O}$ records ⁹ and C) the green circles show the
640 Bermuda Rise $^{231}\text{Pa}/^{230}\text{Th}$ records from core OCE326-GGC5 ⁹ for reference. D) The blue
641 diamonds show the diatom:coccolith ratios from biomarkers ⁵ from the East Equatorial
642 Pacific. E) The solid triangles show the Th-normalised opal accumulation rates from the
643 Southern Ocean ⁴, and the red dotted line shows the EPICA pCO₂ record from Antarctica ⁶³.
644 These records indicate a widespread increase in diatom production and silicon utilisation as
645 a result of an increase in wind-driven upwelling and an increase in thermocline Si(OH)₄
646 concentrations. All error bars show $\pm 2\sigma$ standard deviation. The grey shaded box shows the
647 opal-rich layer of HU890838-8PC; stronger utilization is shown by the darker shading.

648

649 **Tables**

650 Table 1: Summary of sinking opal and sedimentary opal fluxes and indication of preservation
651 efficiency

Parameter	Modern	HS1
Opal sinking flux (mmol Si m ⁻² yr ⁻¹)	50 (From observation)	300 (From fractionation model*)
Th-normalised sedimentary opal flux (mmol Si m ⁻² yr ⁻¹)	~10	~40
Preservation efficiency (%)	~20%	~10-15%

652 **assuming export production is dominated by a bloom of 20-30 days*

653
654 Table 2: A comparison of HS1 and LGM opal burial in the Sargasso Sea (unpublished data
655 from Henry, McManus et al.)

Parameter	HS1	LGM
Percent opal (%)	6.8 ± 0.2 n=5	5.07 ± 0.2 n=9
Th-normalised sedimentary flux (g m ⁻² yr ⁻¹)	3.7 ± 0.2 n=12	5.6 ± 0.4 n=12
Th-normalised sedimentary opal flux (g Si m ⁻² yr ⁻¹)	0.25 ± 0.3 n=12	0.28 ± 0.5 n=12

657





